PB-237 969

ORGANIC COMPOUNDS ENTERING GROUND WATER FROM A LANDFILL

J. Robertson, et al

Oklahoma University

Prepared for:

National Environmental Research Center

September 1974

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INPUT TRANSACTION FORM

3. Accession No. PB 237 969

4. Title
ORGANIC COMPOUNDS ENTERING GROUND WATER FROM A LANDFILL,

7. Author(s)
Robertson, J., Toussaint, C. R., and Jorque, M.

9. Organization
University of Oklahoma
School of Civil Engineering and Environmental Science
Norman, Oklahoma

10. Project No.
21 AKQ, Task 13

11. Contract/Grant No.
R801417

15. Supplementary Notes
U. S. Environmental Protection Agency Report No. EPA-660/2-74-077, September 1974

16. Abstract

Organic compounds leached into ground water from a landfill containing refuse deposited below or near the water table were investigated. Ground water from wells within or near the landfill and a control well was sampled by modified low-flow carbon adsorption procedures incorporating all glass-teflon systems to preclude introduction of extraneous organics. Column chromatography, solubility separation, and gas chromatography-mass spectrometry were employed for separation, identification, and quantitation of individual compounds in organic extracts. The ground water was shown to contain low levels of many undesirable organic chemicals leached from the landfill. Of those compounds identified (over 40), most were chemicals commonly employed in industry for manufacturing many domestic and commercial products. The source of these compounds was apparently manufactured products discarded in the landfill, since it had not received appreciable wastes from industrial operations. Because the age of the refuse in the area studied was at least three years, the compounds identified were believed to be substances leached very slowly from the refuse and/or transported away from the landfill very slowly because of adsorption on aquifer solids. Potential long-term pollution of ground water by industrial organic chemicals from landfills may be indicated by this work.

17a. Descriptors
*Ground water, *Landfills, *Water pollution, *Organic compounds, *Leachate, Water pollution sources, Water pollution control, Organic wastes, Gas chromatograph, Mass spectrometry, Path of pollutants, Activated carbon, Polychlorinated biphenyls, Environmental effects, Aquifers, Sampling, Organic acids

17b. Identifiers
*Carbon adsorption method, Organic Carbon, Refuse, Industrial organic chemicals

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EPA-660/2-74-077
September 1974

ORGANIC COMPOUNDS ENTERING GROUND WATER FROM A LANDFILL

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Grant No. R801417
Project No. 21 AKQ-13
Program Element 1BA024

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Prepared for
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460

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ABSTRACT

Organic compounds leached into ground water from a landfill containing refuse deposited below or near the water table were investigated. Ground water from wells within or near the landfill and a control well was sampled by modified low-flow carbon adsorption procedures incorporating all glass-teflon systems to preclude introduction of extraneous organics. Column chromatography, solubility separation, and gas chromatography-mass spectrometry were employed for separation, identification, and quantitation of individual compounds in organic extracts. The ground water was shown to contain low levels of many undesirable organic chemicals leached from the landfill. Of those compounds identified (over 40), most were chemicals commonly employed in industry for manufacturing many domestic and commerical products. The source of these compounds was apparently manufactured products discarded in the landfill, since it had not received appreciable wastes from industrial operations. Because the age of the refuse in the area studied was at least three years, the compounds identified were believed to be substances leached very slowly from the refuse and/or transported away from the landfill very slowly because of adsorption on aquifer solids. Potential long-term pollution of ground water by industrial organic chemicals from landfills may be indicated by this work.

This report was submitted in fulfillment of Project Number 21 AKQ-13, Grant Number R801417, by the School of Civil Engineering and Environmental Science, University of Oklahoma, under the sponsorship of the U. S. Environmental Protection Agency. Work was completed as of May 1974.

CONTENTS

		Page
Abstract		ii
List of Figures		iv
List of Tables		v
Acknowledgements		vi
Sections		
I	Conclusions	1
II	Recommendations	3
III	Introduction	4
IV	Experimental	7
	Description of the site	7
	Experimental wells	8
	Investigative procedures	8
V	Results and Discussion	21
	Total organic carbon analysis	21
	Initial phase of study	23
	Final phase of study	24
VI	References	45

FIGURES

No.		Page
1	Well Locations at Norman Landfill	9
2	Carbon Adsorption Column for Sampling Ground Water	11
3	Solubility Separation of CAE3II	20
4	Gas Chromatogram of CCE3II, Landfill Well	26
5	Gas Chromatogram of CCEC, Control Well	27
6	Gas Chromatogram of CAE3II, Landfill Well	28
7	Gas Chromatogram of CAEC, Control Well	29

TABLES

No.		Page
1	Maximum BOD and COD Values Obtained from Landfill Leachates	5
2	Fractions Prepared from CCE3II by Silica Gel Column Chromatography	17
3	Fractions Prepared from CCE3II-SG7 by Silica Gel Column Chromatography	18
4	Total Organic Carbon in Ground Water in the Vicinity of the Landfill	22
5	Weights of Carbon Chloroform and Carbon Alcohol Extracts	25
6	Compounds Identified in CCE3II and CAE3II	31

ACKNOWLEDGEMENTS

The Authors wish to express sincere appreciation to William J. Dunlap, whose expert guidance and countless hours of assistance made possible the successful completion of this project.

Special appreciation is due to D. Craig Shew, whose assistance in mass spectrometry was invaluable, and to Marion R. Scalf for advice and assistance in site preparation and drilling of wells.

The patience and assistance of Jack W. Keeley and his willingness to address difficult environmental problems are appreciated in making this project possible.

SECTION I

CONCLUSIONS

1. The landfill investigated in this study was contributing low levels of many undesirable organic chemicals to the ground water with which it was in contact. Principal among the compounds identified were chemicals commonly employed in industry for the manufacture of a wide array of products.

2. Since the refuse in the test area of the landfill had apparently been in place for several years and undergone initial stabilization, the compounds identified in this study were probably those which were leached very slowly from the more intractable refuse and/or which were transported away from the region of refuse deposition very slowly because of significant adsorption on aquifer solids.

3. The introduction of many industrial organic chemicals into ground water by the landfill studied indicates that even those landfills which do not receive appreciable quantities of solid wastes from industrial operations may pollute ground waters with industrial organic compounds, probably by leaching of such substances from finished products manufactured for domestic and commercial use which ultimately are deposited in landfills.

4. The potential for long-term pollution of ground water by industrial organic chemicals from landfills in contact with the water table may be indicated by this study. Such pollution could persist for many years after closing of landfills because of: slow leaching of organic compounds from discarded manufactured products which serve as reservoirs of these compounds; and/or slow "chromatographic" movement of adsorbed, intractable compounds away from the landfill site.

5. If long-term pollution of ground water by landfills does occur it is likely often to be insidious, involving quantities of pollutants too low to noticeably alter the physical properties of the water being degraded. Such pollution is of concern because the effects of long-term ingestion of water containing low levels of organic compounds such as those identified in this study are largely unknown.

6. The compounds identified in this study comprised only a small portion of the total organic matter in the sampled ground water because the carbon chloroform and carbon alcohol extracts prepared by low-flow carbon adsorption apparently contained less than ten percent of the total organic carbon in the water and many of the compounds present in these extracts were not readily amenable to the chromatographic procedures employed in this work.

7. Realistic evaluation of the problem of ground water pollution by organic compounds leached from landfills will require the development of additional information concerning the generation and/or release of organic compounds from refuse, the persistence of such compounds in subsurface environments, and the mobility of recalcitrant organic compounds in ground water aquifers.

SECTION II

RECOMMENDATIONS

1. Comprehensive investigations should be conducted to further elucidate the nature and extent of ground-water pollution by organic compounds leached from landfills. The potential for long-term pollution of aquifers by industrial organic chemicals leached from discarded manufactured products should receive special attention.

2. Methods providing better recovery of organic compounds from ground water than low-flow carbon adsorption should be developed and utilized to obtain improved qualitative and quantitative information in future investigations. The use of macroreticular resins as adsorbents should be explored for this purpose. Also, analytical methods should be expanded to permit study of compounds of higher molecular weight and polarity than those identified in the investigation reported herein.

3. The temporal release of organic compounds from landfill refuse into ground water should be investigated. Variables such as type and compaction of refuse, degree of saturation, oxidation-reduction conditions, and age of the landfill should be correlated with rates of generation and release of organic compounds and identities of these pollutants.

4. The movement and longevity of organic compounds leached from landfills in aquifers of varying geological types should be examined. Consideration should be given to possible slow, "chromatographic" migration through aquifers of zones of pollutants originally concentrated near landfill sites because of significant adsorption on aquifer solids. Information should be developed concerning the persistence in saturated subsurface environments of various classes of organic compounds contributed to ground water by landfills.

5. Information concerning the health effects of long-term ingestion of water containing low levels of organic compounds such as those identified in the study reported herein should be developed as quickly as possible by qualified environmental health science groups. Such information would greatly aid evaluation of the seriousness of the problem of ground water pollution by organic chemicals from landfills, and would also be helpful in assessing other ground-water as well as surface-water pollution problems.

SECTION III

INTRODUCTION

The 1968 National Survey of Community Solid Waste practices in the United States indicated that well over ninety percent of the 800 million pounds of municipal solid waste produced daily was deposited at land disposal sites.[1] A majority of these disposal sites failed to meet the federal and state regulations for sanitary landfills. Open burning was practiced at many of them and placement of solid waste into or near the water table was a common occurrence. In spite of a national effort to improve solid waste disposal methods, over 13,804 open dumps were reported last year (1973).[2] In addition to the obvious pollution caused by open dumps, many of the disposal sites presently designated as sanitary landfills are polluting the nation's precious ground water supplies through direct contact or by the process of leaching. Leaching is the process of dissolving or otherwise placing solids, liquids or gases in solution by the action of water moving through the parent material. Leaching of chemicals from a land disposal site can occur due to direct horizontal flow of ground water or as a result of vertical leaching by percolating water from rainfall or runoff. No accurate figures are available for the amount and severity of ground water pollution by improperly disposed solid waste; however, the few reports on this subject which have been published would suggest that the problem is very serious.

Some recent well-documented cases of ground water pollution from solid waste disposal in California[3], South Dakota[4], and Illinois[5] have indicated that very high concentrations of organic materials may be initially released from landfills located in or near the water table. Landfills receiving substantial amounts of percolation of runoff waters also produced leachates high in organics. The peak production of organics (measured as biochemical oxygen demand, BOD, or chemical oxygen demand, COD) usually occurred within a few months although some landfills required periods of approximately six months to one year for peak production to occur. Examples of BOD and COD values obtained from some of the landfill leachates are shown in Table 1.

Table 1: MAXIMUM BOD AND COD VALUES OBTAINED FROM LANDFILL LEACHATES

Landfill leachate source	BOD mg/liter	COD mg/liter	Reference
Riverside, Cal.	59	-	State of California 1969[3]
Puente, Cal.	9,200	9,280	State of California 1969[3]
Scholl Canyon, Cal.	1,200	5,750	State of California 1969[3]
Blackwell, Ill.	54,610	39,680	Hughes, et.al. 1971[5]
Du Page, Ill.	14,080	8,000	Hughes, et.al. 1971[5]

Variables which were considered to be important factors in the relatively wide range of BOD and COD values obtained include the following: hydrology, geology, topography, type of refuse, and the age of the refuse cell. The hydrological conditions of the areas included widely varying quantities of precipitation and ground water with corresponding effects on rates of leaching. Geological aspects of the areas included such factors as different soil types above and below the cells as well as different types of underground formations present. These characteristics have been shown to greatly influence the ability of water to move through the cells and thus affect leaching rates of organics. In addition, the type of soil would also exert an influence on the amount of adsorption of organic materials. Topographical features of the areas influenced water runoff and percolation rates and consequently affected leaching rates. The types of refuse deposited in the cells exerted a considerable effect on BOD's and COD's produced in leachates since the deposited refuse represented the raw material for this production. For example, a waste high in garbage content would produce high BOD and COD values in leachates rapidly while a waste containing a large percentage of more durable materials such as plastics, paper, and wood would be expected to decompose much more slowly with much lower amounts of BOD and COD being produced. The ages of the refuse cells appeared to be important factors in the quantities of organics present in leachates. An initially high release of organics was usually followed by a much lower release over the next several years.

Experiments involving leaching of refuse in columns, lysimeters and bins have resulted in very high BOD values ranging from 3000 mg/l to > 30,000 mg/l.[6,7] Most of these studies used relatively large volumes of leach water in order to maximize leaching rates. An interesting study was conducted in Britain in which refuse was placed into intermittent and continuous contact with water.[7] In one experiment, deposited

refuse was completely submerged in bins. Horizontal flow of water through the refuse resulted in an accelerated rate of leaching. High initial values of BOD, organic carbon, and organic nitrogen occurred shortly after each new addition of refuse. These wet cells also produced high concentrations of chloride, sulfate, and ammonia.

The studies cited above clearly show that pollution of ground water by organic material leached from land disposal sites can and does occur extensively and is likely to pose a serious threat to ground water quality. Practically no information has previously been developed, however, concerning the nature of the organic pollutants entering ground water as a result of leaching of solid waste, leaving a major gap in the knowledge needed to evaluate the actual extent of the hazard entailed in such pollution. Public land disposal sites have been used extensively until recently for deposition of virtually all of the nation's solid waste including hazardous industrial, hospital, and agricultural waste such as pesticides, plasticizers, solvents, phenolic compounds, and many others. Currently, the bulk of waste from great quantities of products manufactured for domestic and commercial use continues to be placed in land disposal sites, and these products contain or have been produced from a vast array of potentially hazardous organic chemicals. It is obviously important to know if pollution of ground water by leaching of such materials from disposal sites is occurring.

The investigation described in this report consisted of an effort to identify specific organic pollutants contributed to ground water by a landfill near Norman, Oklahoma. The investigation consisted of two principal phases of study. During the initial phase sampling procedures and analytical methods were developed, and organic constituents of ground water obtained from wells in and near the landfill were examined for the presence of polychlorinated biphenyls (PCB's) and subjected to some further study directed towards identification of individual organic compounds present. The PCB's were given special attention because of concern for their hazardous properties and the high probability that most of these compounds and products in which they are used have been deposited in land disposal sites when their useful lives have ended. The data obtained in the identification work in this phase were limited, because of difficulties encountered in sampling the ground water for recovery of organics and the unavailability of analogous organic fractions from a suitable control well for comparison purposes. The second phase, undertaken to correct these deficiencies, was essentially a better controlled, more thorough effort to identify major organic compounds contributed to ground water by the landfill.

SECTION IV

EXPERIMENTAL

DESCRIPTION OF THE SITE

The Norman landfill is located approximately one mile south of the city of Norman, Oklahoma, on the north bank of the South Canadian River in McClain County, Oklahoma. At this point the river's direction is essentially from northwest to southeast and the flow in the river is normally very low except during high rainfall periods.

The water table at the landfill site is quite high, averaging from 2 to 5 ft below the surface in the lower half, adjacent to the South Canadian River. The soil consists of quatenary recent alluvium composed of silt, sand, clay, gravel, and dune sand. All of the soil is moderately or highly permeable. The depth of the alluvial sand layer varies from 35 ft to 40 ft and overlays a 300 ft impervious layer of dense clay and chert gravel, referred to locally as the "red bed".

The landfill was originally operated by the city of Norman for a period of 38 years as a dump in which there was no restriction concerning the type of material disposed of and in which open burning was practiced. During flood periods, the landfill was partially inundated by flood waters. The river bank in at least one place was eroded by flood waters so that old debris is now visible on the bank. No flooding has occurred in recent years because of upstream flood control dams.

Beginning in 1960, large quantities of refuse were placed in trenches approximately 10 ft deep which had been dug by a dragline to obtain sand for a sand and gravel company. These trenches intercepted the water table in many places since the ground water is within a few feet of the surface in a large portion of the landfill area. In this operation, garbage trucks dumped their loads near the working end of each trench. A bulldozer then pushed a layer of refuse approximately 12 ft thick over and into the trench which contained as much as 5 to 8 ft of water. The deposited material was later covered with approximately 6 in of cover material. Cover material used was that available at the site, and was essentially a fine, permeable sand as described earlier in this section.

The trench type of operation was carried out from approximately 1960 to the spring of 1972 when new state solid waste legislation required the operators to change the method of operation to a modified area fill in order to help prevent further ground water contamination. In this

method, solid wastes were deposited in layers at least 2 ft above the water table and covered at least weekly.

Within the past year, the deposited wastes have been covered almost daily and, at the present time, the site is classified as a sanitary landfill. The newer portion of the landfill has been in operation approximately 15 years.

The direction of ground water flow at the newer landfill was determined in the spring of 1972.[8] The direction of flow of ground water was considered to be normal to the contours and approximately 7° west of south.

EXPERIMENTAL WELLS

Four wells were used in this study. Three of these were test wells in or adjacent to the new landfill site. The fourth well was a control well located approximately one mile northwest of the landfill site. The locations of test wells No. 2, 3, and 4 are shown in Figure 1. Well No. 4 was drilled in April of 1972, and cased with galvanized iron pipe to a depth of 15 ft. It was perforated from 9 to 15 ft and held 12 ft of standing water. Well No. 2 was drilled in November, 1971, and cased to a depth of 40 ft with 38.5 ft of water. The lower 10 ft were perforated. Well No. 3 was drilled in November, 1972, in the southeastern portion of the new landfill where the age of the refuse was approximately three years. This well was drilled through a refuse layer 20 to 22 ft thick. The total depth of well No. 3 was 32 ft and the lower 12 ft were perforated. It contained 17 ft of standing water. The control well was drilled in October, 1973 , and was cased to 42 ft. It was perforated in the bottom 12 ft and held 37 ft of standing water. Well No. 2 and the control well were drilled to the "red bed". Wells No. 3 and 4 were not drilled to the "red bed" but did have solid iron plates at the bottom to prevent sand intrusion. All of the wells were gravel packed with fine gravel and coarse sand to help prevent the surrounding sand from filling them. The packing also allowed surrounding ground water to flow into the wells at faster rates. Each of the wells was thoroughly bailed and pumped initially after drilling and was also pumped prior to sampling.

INVESTIGATIVE PROCEDURES

General Procedures

Stringent precautions were exercised throughout the investigation to prevent contamination of samples with extraneous organic matter. Only pesticide grade solvents or analytical reagent grade solvents which were redistilled in glass were used. All glassware was subjected to a

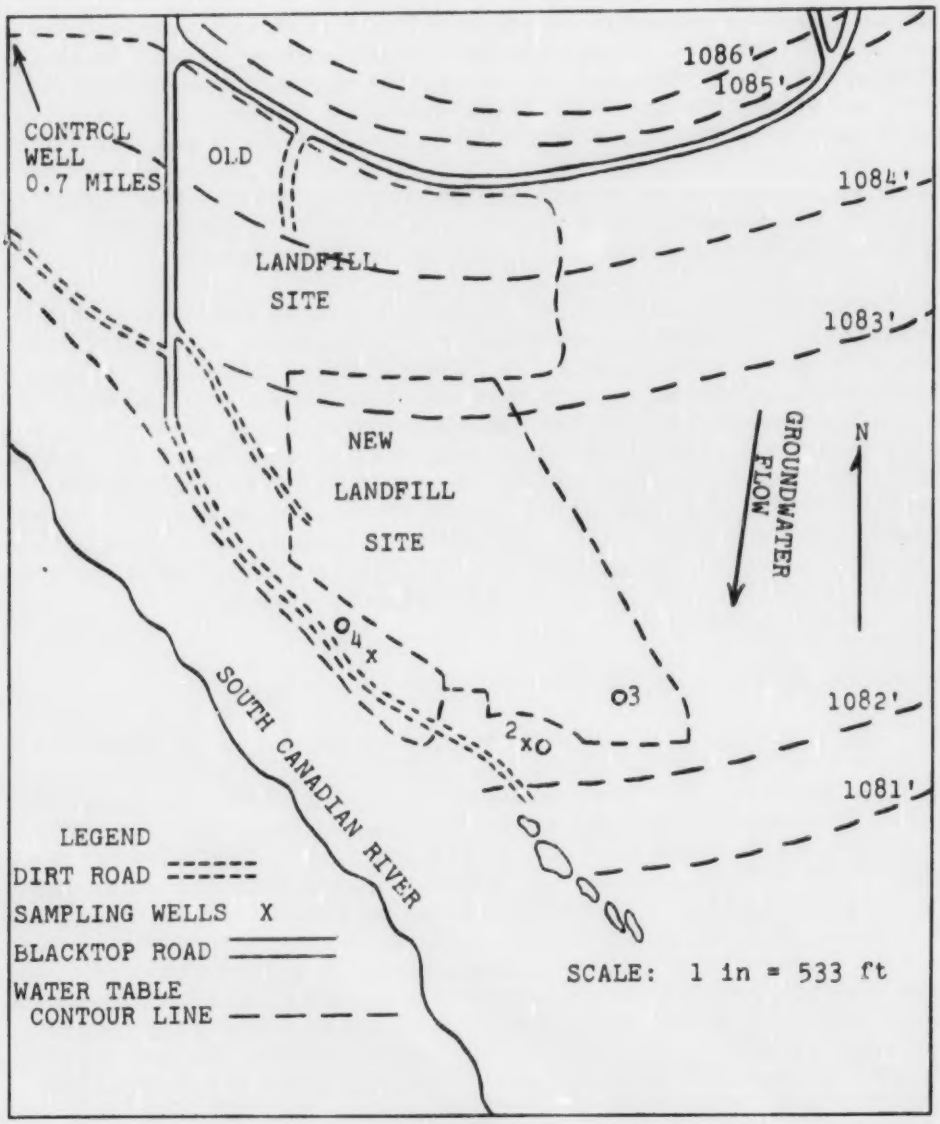

FIGURE 1. WELL LOCATIONS AT NORMAN LANDFILL

rigorous cleaning procedure which entailed: thorough washing with detergent solution; rinsing with tap water; soaking in dichromate cleaning solution; thorough tap water rinsing; multiple rinsing with distilled water; rinsing with glass-distilled acetone; and oven drying. Sample materials were allowed to contact only clean glass and Teflon.

Ground water samples were analyzed at various times during both phases of the investigation for total dissolved organic carbon, employing a Dow-Beckman Carbonaceous Analyzer (single channel).[9]

Gas chromatographic analysis of organic fractions obtained in the investigation was achieved by means of Varian Model 204B and Varian Model 2100 gas chromatographs. A Finnigan Model 1015C gas chromatograph-mass spectrometer with both electron impact and chemical ionization sources and Systems Industries System 150 data system was employed for collecting and processing mass spectral data for various organic fractions isolated during the studies. Computerized mass spectra matching programs based on libraries of mass spectra at the National Institutes of Health, Bethesda, Maryland, and Battelle Memorial Institute, Columbus, Ohio, were utilized in evaluating mass spectral data for identification of individual organic compounds.[10]

Procedures Employed in the Initial Phase of Study

Sampling Procedures - Organic components in ground water from well No. 3, within the new landfill, and well No. 2, downstream from the landfill near its edge, were sampled for analysis in this phase of study. The sampling procedures employed during most of this work incorporated a modified version of the low-flow carbon adsorption method[11,12], with the ground water being pumped from the saturated zone directly through columns containing activated carbon to adsorb and recover the organic compounds. Glass columns 3 in X 18 in were employed (Figure 2). They were constructed from 3 in diameter Pyrex drain line and could be disassembled for packing and unloading, with the two sections being held together by a Pyrex drain pipe coupler with a Teflon gasket. Columns were plugged at both ends with solvent-extracted glass wool and were packed with 30 mesh activated carbon (Nuchar C-190, Plus 30, Herbert Chemical Co., St. Bernard, Oh.).

For sampling, a packed column was placed in a vertical position at the top of the casing of the well to be sampled. A suitable length of Teflon tubing was attached to the bottom inlet of the column and extended down the well shaft into the saturated zone. The ground water was then pumped up the tubing and through the carbon column by an impeller type (centrifugal) pump attached by Teflon tubing to the outlet (downstream) end of the column. Flow rates and quantities of water sampled were determined by collecting the discharge water from the pump in suitable containers and measuring the volume.

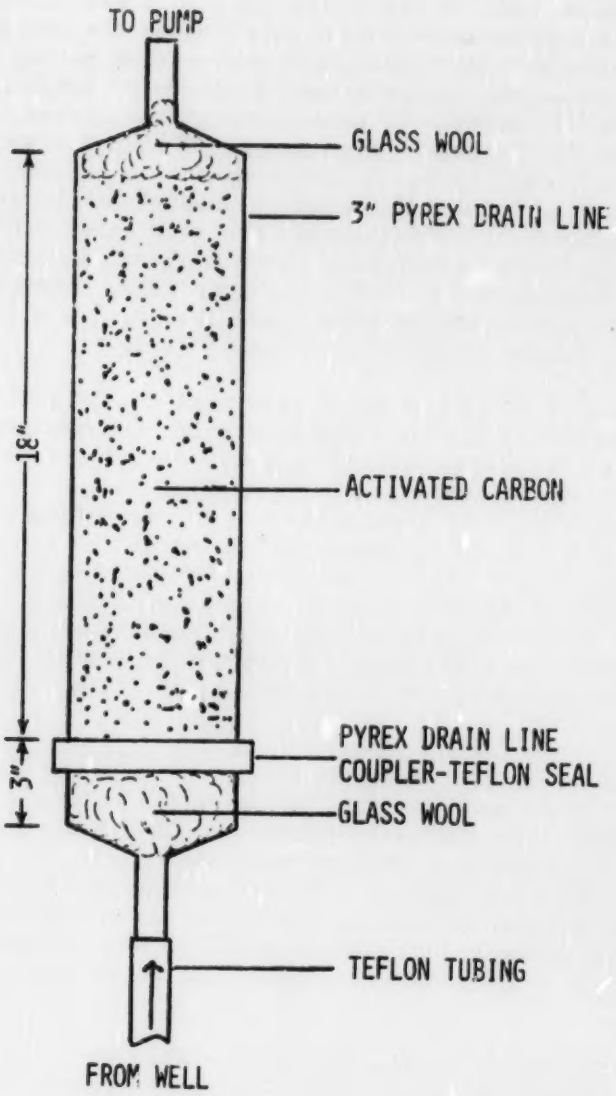

FIGURE 2. CARBON ADSORPTION COLUMN FOR SAMPLING GROUND WATER

The use of an all glass and Teflon system from the saturated zone to the outlet of the carbon adsorption column and placement of the pump on the downstream side of the column virtually precluded introduction of any organic contaminants during sampling of the ground water. However, considerable difficulty was encountered during this phase of the study in attempting to attain desired low rates of flow (approximately 100 ml/min) of water through the carbon columns when using impeller (centrifugal) type pumps. Although several pumps of this type were tried, including those operating on both A.C. and D.C. current, none was found capable of sustained operation at the low flow rate needed. Consequently, the flow rates achieved in carbon adsorption sampling of the ground water analyzed in this phase of study were non-uniform and higher than optimum. These flow rates and the volumes of water sampled were: well No. 2, 400 ml/min, 100 gal (379 l); well No. 3, 175 ml/min, 42 gal (159 l).

Organic compounds in ground water from well No. 3, within the landfill, were also sampled during this phase of study by sorption on Amberlite XAD-2, an insoluble cross-linked polystyrene polymer supplied as 20-50 mesh beads (Rohm and Haas Co., Philadelphia, Pa.). This method was reported by Harvey to be very effective in recovering PCB's from aqueous samples.[13] A 3 X 21 cm column of XAD-2 containing 150 cm^3 of the resin was employed. Before the column was packed, the resin was washed with several volumes of distilled water, extracted twice for 18 hr each time in a Soxhlet extractor with acetonitrile, and finally washed thoroughly with additional distilled water to remove the acetonitrile. A glass wool plug was placed at the inlet end of the column to serve as a pre-filter.

Because of clogging problems, ground water could not be pumped directly from the saturated zone through the amberlite column. Instead, ground water was drawn from the water table through a Teflon tube into a closed carboy at the well head by maintaining a vacuum in the carboy. Five gallons of water were then filtered through a prewashed glass fiber filter and passed through the resin column at full gravity flow. The flow rate through the column was 100 ml/min, initially, but had decreased to 60 ml/min when passage of the water sample neared completion.

Desorption of Sampled Organic Material - When sampling was completed the carbon adsorption columns were drained to remove excess water. The carbon containing the organic material adsorbed from the sampled water was then dried carefully by passing nitrogen through the columns for approximately 24 hr while heating gently at temperatures not exceeding 65°C. The dried carbon from each column was transferred to modified, large-size (220 ml) Soxhlet extractors and extracted with chloroform for 36 hr. The carbon chloroform extracts (CCE's) obtained were filtered through solvent-extracted glass fiber filters to remove any carbon fines present, and were concentrated at low temperature under

vacuum in rotary evaporators. The CCE's from ground water from wells No. 2 and No. 3 were designated CCE2 and CCE3, respectively.

Upon completion of the sampling procedure using Amberlite XAD-2, the column was drained of excess water and the glass wool pre-filter was removed. Organic compounds adsorbed on the resin were eluted by successively passing 200 ml of hot ethanol and 500 ml of distilled water through the column at full gravity flow. The combined ethanol-water eluate was extracted three times with 50 ml portions of hexane. The hexane extracts were combined, dried with anhydrous sodium sulfate, and carefully concentrated to a volume of 5 ml in a rotary evaporator.

Analysis of Organic Extracts - Both CCE2 and CCE3 were subjected to liquid-solid chromatography on columns of silica gel to obtain fractions of less complexity for further study. These CCE's were chromatographed on 12 X 15 cm columns dry-packed with 100-200 mesh Silicar CC-7 (Mallinckrodt Chemical Works, St. Louis, Mo.) which were eluted successively with 200 ml each of hexane, benzene, chloroform, and a mixture of chloroform-methanol (1:1, v/v). Eight 100 ml fractions were collected, with each of the four eluting solvents producing two fractions.

The CCE silica gel fractions and the hexane extract prepared from the Amberlite XAD-2 eluate were subjected to gas chromatography on the following columns: 5.3% DC-200 on 80/100 mesh Gas Chrom Q (Applied Science Laboratories, State College, Pa.); 3% OV-1 on 100/120 mesh Gas Chrom Q; and, 10% QF-1 on 80/100 mesh Gas Chrom Q. The chromatograms obtained were compared with chromatograms produced under the same conditions by a series of standard PCB's (Arochlor 1232, 1242, 1248, 1254, 1260, and 1262). Those fractions which appeared, on the basis of the retention times of their constituent compounds, possibly to contain PCB's were further investigated by combined gas chromatography-electron impact mass spectrometry (GC-MS) with computerized data acquisition and processing. Spectra of the compounds indicated by their gas chromatography retention times as possible PCB's were individually examined. The acquired data were further examined by the limited mass search technique in order to detect any spectra containing ion fragments characteristic of PCB's. Spectra found to contain such fragments were then examined in their entirety. Finally, the combined benzene fractions from both CCE2 and CCE3 were subjected to a GC-MS procedure involving selected ion monitoring during the data acquisition step in order to attain enhanced sensitivity for the detection of PCB's.[15]

Further investigation of the hexane and benzene fractions obtained by silica gel column chromatography of CCE's 2 and 3 was then undertaken in an effort to characterize compounds comprising a significant portion of these fractions. Mass spectra obtained by GC-MS of the various fractions were examined by standard interpretive procedures based on mass spectral fragmentation theory and by computerized spectral matching programs which permitted comparison of the unknown spectra with the

contents of the mass spectral libraries at Battelle Columbus and National Institutes of Health. Identifications of compounds in the CCE fractions achieved by mass spectral interpretation or matching were further substantiated, when standards were available, by directly comparing the behavior during gas chromatography and GC-MS of the CCE compounds with that of standard compounds under identical conditions.

Procedures Employed in the Final Phase of Study

Sampling Procedures - Ground waters from well No. 3, within the landfill, and a newly drilled control well located approximately one mile from the upstream edge of the landfill and 1.5 miles from well No. 3, were sampled for organic components during this phase of the study. The wells were sampled simultaneously and by identical procedures in order that comparison of organic matter from the control and landfill wells would clearly reveal the extent and nature of organic contamination of ground water by the landfill and provide a guide for selection of compounds which should receive priority attention in identification studies.

The sampling procedures employed were essentially those developed in the initial phase of study which were based on the low-flow carbon adsorption method. However, the carbon columns differed from those used in the first phase of study in that they incorporated no joints, but were single piece units fabricated from single lengths of 3 in diameter Pyrex glass tubing. This one-piece design was used to eliminate the possibility of any leakage of air into the columns through joints, since occasional small leaks were observed around the Teflon gaskets of the couplers for the two-piece columns used in the initial work. Also, the centrifugal pumps employed in the initial studies were replaced by variable speed peristaltic type pumps ("Masterflex" 7545 Variable Speed Drive with 7014 pump head, Cole-Parmer Instrument Co., Chicago,Ill.) which permitted sustained pumping of ground water from the water table through carbon adsorption columns at accurately controlled, constant, low flow rates. Power was provided to the pumps at the field sites by portable gasoline-operated 1500 watt AC generators.

Sampling was accomplished by pumping ground water from each of the two wells through essentially identical carbon columns for 126 hr at a rate of 100 ml/min. In this manner 200 gal (757 l) of water was sampled at each location.

Desorption of Sampled Organic Material - Upon completion of sampling the carbon columns containing the adsorbed organics from the water from well No. 3 and the control well were drained to remove excess water, sealed with solvent washed aluminum foil, and transported immediately to the laboratory for processing. A third carbon column which had been

prepared identically and at the same time as the columns used for sampling, but which had not had any water passed through it, was processed with the sampling columns to serve as a blank.

The glass columns were scored with a glass saw, and then were carefully broken open to permit removal of the carbon in a special carbon-handling room designed to minimize the potential for contamination of the carbon during processing. The carbon was carefully transferred to Pyrex glass dishes and dried at approximately 40°C for 48 hr under a gentle flow of clean air in a Precision-Freas mechanical convection oven (Model 845, Precision Scientific Company, Chicago, Ill.). The air inlet of the oven was equipped with a carbon filter to prevent contamination from the atmosphere.

The dried carbon was transferred to 2200 ml modified Soxhlet extractors and extracted for 48 hr with chloroform. The CCE's obtained from the blank carbon and the carbon employed in sampling well No. 3 and the control well were designated CCEB, CCE3II, and CCEC, respectively. These extracts were filtered through solvent-extracted glass fiber filters to remove carbon fines and then vacuum concentrated at temperatures not exceeding 27°C in rotary evaporators to a final volume of 3 ml each.

The chloroform-extracted carbon samples were dried in the Soxhlet extractors by passing a gentle stream of warm, dry air through the extraction chambers via the siphon tubes for 20 hr. The carbon was then extracted for 32 hr with pure ethanol, and the carbon alcohol extracts (CAE's) were filtered and concentrated in the same manner as the CCE's. However, it was necessary to filter the CAE's through extracted glass fiber filters when volumes of about 10 ml had been attained in order to remove precipitated material. These precipitates, together with solid material which had precipitated on the flask walls during evaporation, were dried and weighed. The filtered CAE's were then further evaporated to the following final volumes: 4.0 ml for CAE3II, from well No. 3; 2.0 ml for CAEC, from the control well; and, 1.0 ml for CAEB, from the blank.

Analysis of Organic Extracts - Aliquots of each of the concentrated CCE's and CAE's were carefully evaporated to dryness in tared foil cups in order to determine the weights of soluble material dissolved in the concentrates. The total weights of the CCE's and CAE's were calculated from these weights and the weights of material which had precipitated during preparation of the concentrated extracts.

CCE3II and CAE3II, prepared from water from the landfill well, were compared by gas-liquid chromatography on an OV-1 column under identical operating conditions with corresponding CCE's and CAE's from the control well water and carbon blank. This comparison indicated those organic substances readily amenable to gas chromatography in CCE3II and CAE3II that had been contributed to ground water by the landfill and provided

a basis for selection of subsequent analytical steps employed in analysis of these extracts.

CCE3II was subjected to liquid-solid chromatography on micro silica gel columns to obtain fractions of less complexity for further study. Initially, a 7 X 76 mm column of 100/200 mesh Silicar CC-7 was prepared by dry packing and subsequent washing with hexane to wet the column and determine the void volume. A 1.5 ml aliquot of CCE3II was charged to the column by carefully adsorbing it on a small portion of Silicar CC-7, suspending the Silicar containing the adsorbed CCE in a small quantity of hexane, and carefully placing this suspension on top of the column. The column was eluted successively with 8 ml each of hexane, benzene, and chloroform-methanol (1:1), followed by 5 ml of methanol. The fractions of 2 or 3 ml each were collected after a volume of hexane equivalent to the void volume had been eluted. These fractions were designated CCE3II-SG1 through 10 as shown in Table 2.

The 10 fractions from the silica gel column were each carefully concentrated to a volume of 1 ml in a rotary evaporator. The concentrated fractions, together with the hexane representing the void volume of the column, were then examined by gas chromatography on OV-1. Fractions CCE3II-SG4, 5, 6, and 7 were found to contain sufficient quantities of organic compounds to warrant further study, with fractions SG4, 5,and 6 appearing amenable to conclusive investigation by GC-MS without additional purification. Fraction CCE3II-SG7, which contained a very significant portion of the organic compounds of the parent CCE, was quite complex and hence was rechromatographed on a fresh 7 X 76 mm column of Silicar CC-7. Elution was accomplished with a total volume of 370 ml of solvent ranging in polarity from hexane to methanol, with 26 fractions being collected as shown in Table 3. Collection of fractions and the sequence of eluting solvents were based partially on the movement from the column of fluorescent zones which were detected under 366 nm U.V. light. The fractions were examined by gas chromatography on an OV-1 column, and several groups of fractions which appeared to contain very little organic matter or low levels of essentially the same components were recombined, as indicated in Table 3. All fractions were concentrated to approximately 1 ml each by rotary evaporator and then examined by gas chromatography on columns packed with 3% OV-1 and 3% Carbowax 20M to develop experimental conditions for use in GC-MS studies.

The various fractions obtained by silica gel column chromatography of CCE3II were analyzed by GC-MS to achieve identification of individual compounds therein. Essentially the same procedures were employed as in the previously described initial phase of this study, except that fractions were subjected to chemical ionization as well as electron impact mass spectrometry in order to gain additional information of considerable value in structural characterization. Standard mass

Table 2: FRACTIONS PREPARED FROM CCE3II BY SILICA GEL COLUMN CHROMATOGRAPHY

Fraction	Total volume	Eluting solvents
CCE3II-SG1	2 ml	Hexane
CCE3II-SG2	3 ml	Hexane
CCE3II-SG3	3 ml	Hexane
CCE3II-SG4	2 ml	Benzene
CCE3II-SG5	3 ml	Benzene
CCE3II-SG6	3 ml	Benzene
CCE3II-SG7	2 ml	Chloroform-Methanol (1:1)
CCE3II-SG8	3 ml	Chloroform-Methanol (1:1)
CCE3II-SG9	3 ml	Chloroform-Methanol (1:1)
CCE3II-SG10	5 ml	Methanol

Table 3: FRACTIONS PREPARED FROM CCE3II-SG7 BY SILICA GEL COLUMN CHROMATOGRAPHY

Fraction	Total volume	Eluting solvents
CCE3II-SG7-SG1[a]	10 ml	Hexane
" SG2[a]	10 ml	Hexane
" SG3[a]	10 ml	Hexane
" SG4[b]	10 ml	Hexane
" SG5[b]	15 ml	Hexane,10 ml Hexane-Benzene(1:1),5 ml
" SG6[b]	15 ml	Hexane-Benzene(1:1)
" SG7	15 ml	Hexane-Benzene(1:1)
" SG8	15 ml	Hexane-Benzene(1:1),5 ml Hexane-Benzene(1:3),10 ml
" SG9[c]	15 ml	Hexane-Benzene(1:3),10 ml Benzene,5 ml
" SG10[c]	15 ml	Benzene
" SG11[c]	15 ml	Benzene
" SG12	15 ml	Benzene
" SG13	15 ml	Benzene-Chloroform(3:1)
" SG14[d]	15 ml	Benzene-Chloroform(3:1)
" SG15[d]	15 ml	Benzene-Chloroform(3:1),10 ml Benzene-Chloroform(1:1),5 ml
" SG16[d]	15 ml	Benzene-Chloroform(1:1)
" SG17[d]	15 ml	Benzene-Chloroform(1:1)
" SG18[d]	15 ml	Benzene-Chloroform(1:1),5 ml Benzene-Chloroform(1:3),10 ml
" SG19[d]	15 ml	Benzene-Chloroform (1:3)
" SG20[d]	15 ml	Benzene-Chloroform(1:3)
" SG21	15 ml	Chloroform
" SG22	15 ml	Chloroform
" SG23[e]	15 ml	Chloroform,5 ml Chloroform-Methanol(1:1),10 ml
" SG24[e]	15 ml	Chloroform-Methanol(1:1)
" SG25[e]	15 ml	Methanol
" SG26[e]	15 ml	Methanol

a Recombined as CCE3II-SG7-SG1→3.
b Recombined as CCE3II-SG7-SG4→6.
c Recombined as CCE3II-SG7-SG9→11.
d Recombined as CCE3II-SG7-SG14→20.
e Recombined as CCE3II-SG7-SG23→26.

spectral interpretative procedures and computerized spectral matching programs were utilized for examination of spectra, and additional corroborative evidence for the structures of compounds identified on the basis of their spectra was obtained by direct comparison with standard compounds whenever such standards were available. When possible, the quantities of the identified compounds in the original CCE and various fractions obtained from it were estimated by comparing their peak heights on gas chromatograms with the peak heights produced by known quantities of standard compounds chromatographed under identical conditions. These data were then used to calculate estimated concentrations of the identified organic compounds in the sampled ground water.

CAE3II, the carbon alcohol extract from well No. 3, was separated into fractions of less complexity by classical solubility separation procedures.[16,17] A 1.5 ml aliquot of the concentrated CAE (total volume 4 ml) was dissolved in 30 ml of diethyl ether, filtered, and extracted successively with water, dilute hydrochloric acid, and dilute sodium hydroxide, as shown in Figure 3. Five fractions, namely ether insolubles, water solubles, bases, acids, and neutrals were obtained.

The ether insolubles fraction contained an appreciable quantity of material (0.3 g), while the water solubles fraction was of lesser, but still significant, weight (0.05 g). However, because of the polarity and probable complexity of these fractions and time limitations on this investigation, no further studies of the ether insolubles and water solubles were conducted.

The bases, acids, and neutrals fractions were dried on anhydrous sodium sulfate columns and concentrated to 1-2 ml each in rotary evaporators. Examination of these fractions by gas chromatography on an OV-1 column indicated that the acids fraction, designated CAE3II Acids, contained a total quantity of organic compounds several orders of magnitude greater than that present in the other fractions. Hence, the acids fraction was selected for further study.

The CAE3II Acids fraction was subjected to gas chromatography and GC-MS, employing columns packed with 10% SP1200/1% H_3PO_4 on 80/100 mesh Chromasorb W AW (Supelco, Inc., Bellefonte, Pa.). Both electron impact and chemical ionization mass spectrometry were utilized, and procedures for identification and quantitation of individual compounds were essentially identical with those employed for the CCE3II compounds as previously described.

A small aliquot of the CAE3II Acids fraction was allowed to react with 14% boron trifluoride in methanol[18] to esterify carboxylic acids and, hence, permit detection and quantitation of any acids of higher molecular weight which might be present. However, time limitations permitted only a cursory examination by gas chromatography of this methylated fraction.

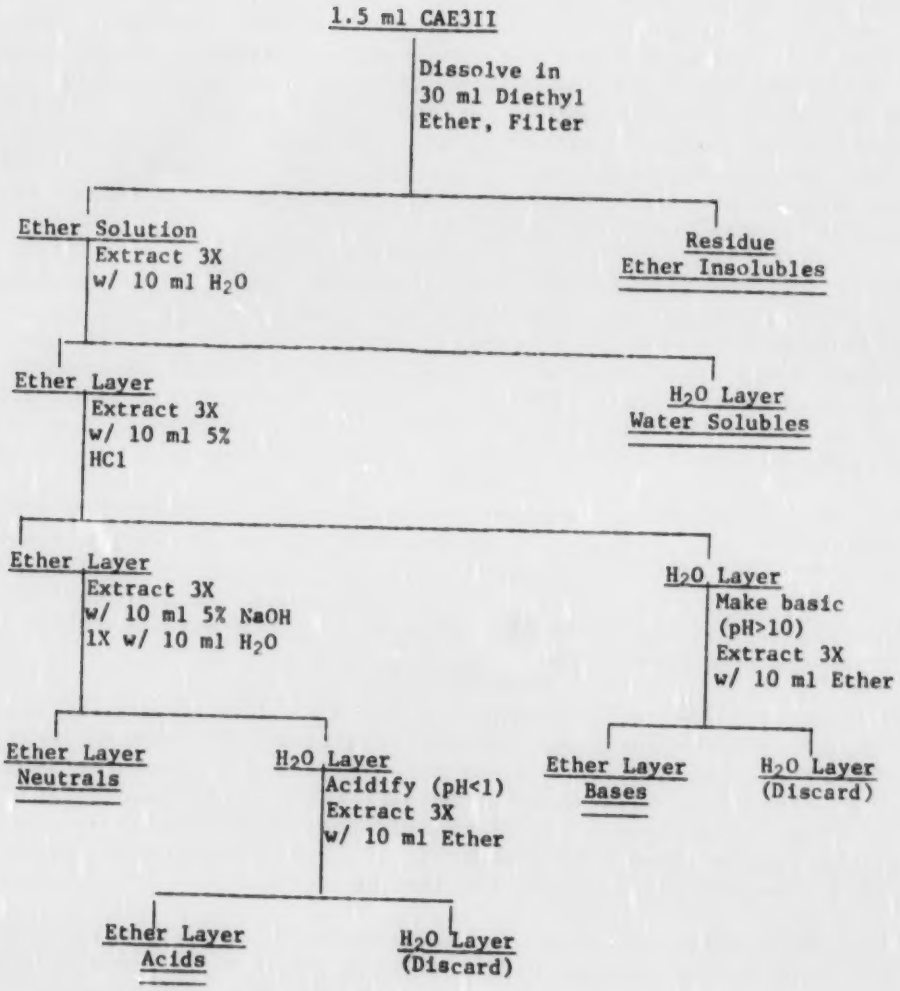

FIGURE 3. SOLUBILITY SEPARATION OF CAE3II

SECTION V

RESULTS AND DISCUSSION

TOTAL ORGANIC CARBON ANALYSIS

Table 4 presents data for total dissolved, non-volatile carbon analyses of water from: well No. 3, within the landfill; well No. 2, at the edge of the landfill approximately 230 ft southwest of well No. 3; well No. 4, at the edge of the new landfill approximately 865 ft west northwest of well No. 3; and the control well, approximately one mile from the northwest edge of the landfill. The data for wells No. 2 and 4 for May, 1972, were obtained by other investigators before the beginning of this study.

These data indicate relatively low levels of organic carbon in ground water in and near the landfill. Water from well No. 3, within the landfill, showed a maximum TOC of only 34.2 mg/l and a minimum of 11.1 mg/l. Analogous data for wells No. 2 and 4, on the periphery of the landfill, were respectively: 23.0 and 5.5 mg/l; and, 28.0 and 8.0 mg/l. Loss of volatile organic compounds during removal of carbonate from the samples prior to TOC determination may have reduced the values obtained to some extent. Most likely, however, the relatively low TOC values reflect the age of the landfill in the vicinity of the wells where sampling of ground water was accomplished. Newspapers recovered from well No. 3 during drilling indicated the solid waste in this region of the fill had been in place for at least three years. Hence, the major portion of readily leachable organic matter would almost undoubtedly have long since been removed from the waste, and only those organic compounds which leached very slowly from the solids in the landfill or which persisted for considerable periods of time in the immediate vicinity of the landfill after being released from the solid refuse would have been present by the time this study was undertaken.

The considerable temporal fluctuations of TOC's in ground water from the various wells probably resulted from climatic factors. During the first five months of 1973 unusually high rainfall occurred in the Norman area. Hence, the higher TOC in water from well No. 3, within the landfill, may have resulted from both a higher water table, which brought more waste within the zone of saturation, and increased vertical leaching from unsaturated refuse. Similarly, the reduced TOC's in water from wells No. 2 and 4, outside of the fill, may have reflected dilution by high levels of fresh recharge water. The increased levels of organic carbon in wells 2 and 4 in August may simply reflect decreased fresh water recharge accompanying dry weather conditions, coupled with the arrival at these wells of water containing higher quantities of organic matter leached from the landfill during the earlier very wet period. Similarly, by August a decreasing water

Table 4: TOTAL ORGANIC CARBON IN GROUND WATER IN THE VICINITY OF THE LANDFILL (mg/l)

Well No.	Location	TOC (Filtered) 5/6/72	6/6/73	8/10/73	9/28/73	5/24/74
2	Edge of the landfill, 230 ft southwest of well No. 3	9.0	5.5	23.0	13.2	b
3	In the landfill	a	34.2	13.0	16.3	11.1
4	Edge of landfill, approximately 865 ft west northwest of well No. 3, in old dump area	13.0	8.0	28.0	-	-
Control	Approximately one mile northwest of landfill edge	c	c	c	c	4.6

a Well drilled 11/15/72.
b Well inadvertantly destroyed by landfill operator in January, 1974.
c Well drilled 10/15/73.

table and less vertical leaching likely combined to result in a lower level or organic carbon in well No. 3.

INITIAL PHASE OF STUDY

Analysis for PCB's

The hexane and benzene fractions obtained by silica gel column chromatography of the CCE's from wells No. 2 and 3 and the hexane fraction prepared by sampling well No. 3 with Amberlite XAD-2 all contained substances which, on the basis of their GC retention times, could have been PCB's. Mass spectra of these compounds clearly showed, however, that none of them were PCB's. Evaluation of GC-MS data from the various fractions by limited mass search techniques and utilization of GC-MS procedures involving selected ion monitoring for further examination of the silica gel column fractions likewise failed to produce any evidence to indicate the presence of PCB's in ground water in or near the landfill. The minimum concentration of PCB's which the methods employed in this study could have detected in the sampled ground water is conservatively estimated to be 50 ng/l.

The failure to detect PCB's in the ground water in and near the Norman landfill is not surprising. These compounds are very insoluble in water and tend to be adsorbed very strongly to soil. It is probable, then, that PCB's introduced into the landfill would be largely adsorbed on soil particles within a short distance of the point of deposition. The quantities of PCB's in the adjacent water would then be functions of the distribution coefficients for the various isomers in a soil-water system, and these coefficients are undoubtedly very highly weighted toward the soil phase. Some slow diffusion of PCB's outward from the landfill could occur over a period of years, but the proportion present in the ground water would probably remain so minute as to be undetectable and probably not environmentally significant.

Characterization of Other Organic Compounds

Data obtained by GC-MS of the hexane fractions prepared by silica gel column chromatography of CCE3 indicated that these fractions probably contained a mixture of aliphatic hydrocarbons as well as some elemental sulfur. Gas chromatographic analysis of analogous fractions from CCE2 indicated them to be essentially identical in composition to the CCE3 hexane fractions. Identification of individual compounds from these rather complex fractions would have required extensive additional preparative work, and was not attempted during this investigation.

Mass spectra of several of the more predominant compounds in the silica gel benzene fractions from both CCE2 and 3 indicated these substances

to be esters of dicarboxylic acids, particularly phthalic acid. Four of these were identified with reasonable certainty on the basis both of their mass spectra and GC retention times as diethyl phthalate, diisobutyl phthalate, dioctyl phthalate, and dioctyl adipate. Two others were tentatively identified as di-n-butyl phthalate and butyl-carbobutoxymethyl phthalate. All of these diesters were present in the benzene fractions from both CCE2 and 3. Concentrations appeared to be generally higher in CCE3, however.

Some evidence was also obtained for the presence of two cresols in the CCE3 benzene fractions.

FINAL PHASE OF STUDY

Comparison of CCE's and CAE's from Well No. 3, Control Well, And Carbon Blank

Visual comparison of the various CCE's and CAE's showed CCE3II, prepared from ground water from well No. 3, to be deep yellow in color, while CCEC, from the control well water, was light yellow, and CCEB, from the carbon blank, was practically colorless. Similarly, CAE3II was deep yellow-orange, CAEC was yellow, and CAEB was pale yellow. Both CCE3II and CAE3II were very odorous, while the control and blank CCE's and CAE's were essentially odorless.

Table 5 presents the weights, in terms both of total weight and weight per liter of sampled water, of the various CCE's and CAE's. As these data show, CCE3II contained approximately 25 times as much material as CCEC and more than 100 times the weight of material in CCEB, while CAE3II contained in the neighborhood of four times the quantity of material contained by CAEC and CAEB, the control and blank.

The observations and data presented above clearly indicated the presence of much greater quantities of organic constituents in the ground water in the locale of the Norman landfill than in ground water from the same aquifer approximately one mile upstream from the landfill perimeter. This situation was further illustrated by comparison of the various CCE's and CAE's by gas chromatography, as shown in Figures 4 through 7. These chromatograms were obtained by chromatographing, under identical conditions, aliquots of CCE3II and CCEC representing 190 ml of ground water from well No. 3 and the control well, respectively, and aliquots of CAE3II and CAEC representing 380 ml of ground water from these wells. Analogous chromatography of suitable aliquots of CCEB and CAEB, from the carbon blank, produced chromatograms which are not shown here but which were very similar to those obtained for CCEC and CAEB. These chromatographic comparisons revealed in the ground water from the landfill the presence of a complex array of organic compounds which were readily amenable to gas chromatography and which were either not present, or were present in very much less quantity, in ground water not subject to the influence of the landfill.

Table 5: WEIGHTS OF CARBON CHLOROFORM AND CARBON ALCOHOL EXTRACTS

Source	Weight of CCE		Weight of CAE		Weight of CCE+CAE		Weight of activated carbon in column, g
	Total, mg	mg/l	Total, mg	mg/l	Total, mg	mg/l	
Well No. 9	304.5	0.402	1219.1	1.610	1523.6	2.013	274
Control Well	11.9	0.016	314.2	0.415	326.1	0.431	255
Carbon Blank	2.6	0.003[a]	262.5	0.347[a]	264.8	0.350[a]	213

a Calculated as if this carbon had actually been employed for sampling of 757 l of water.

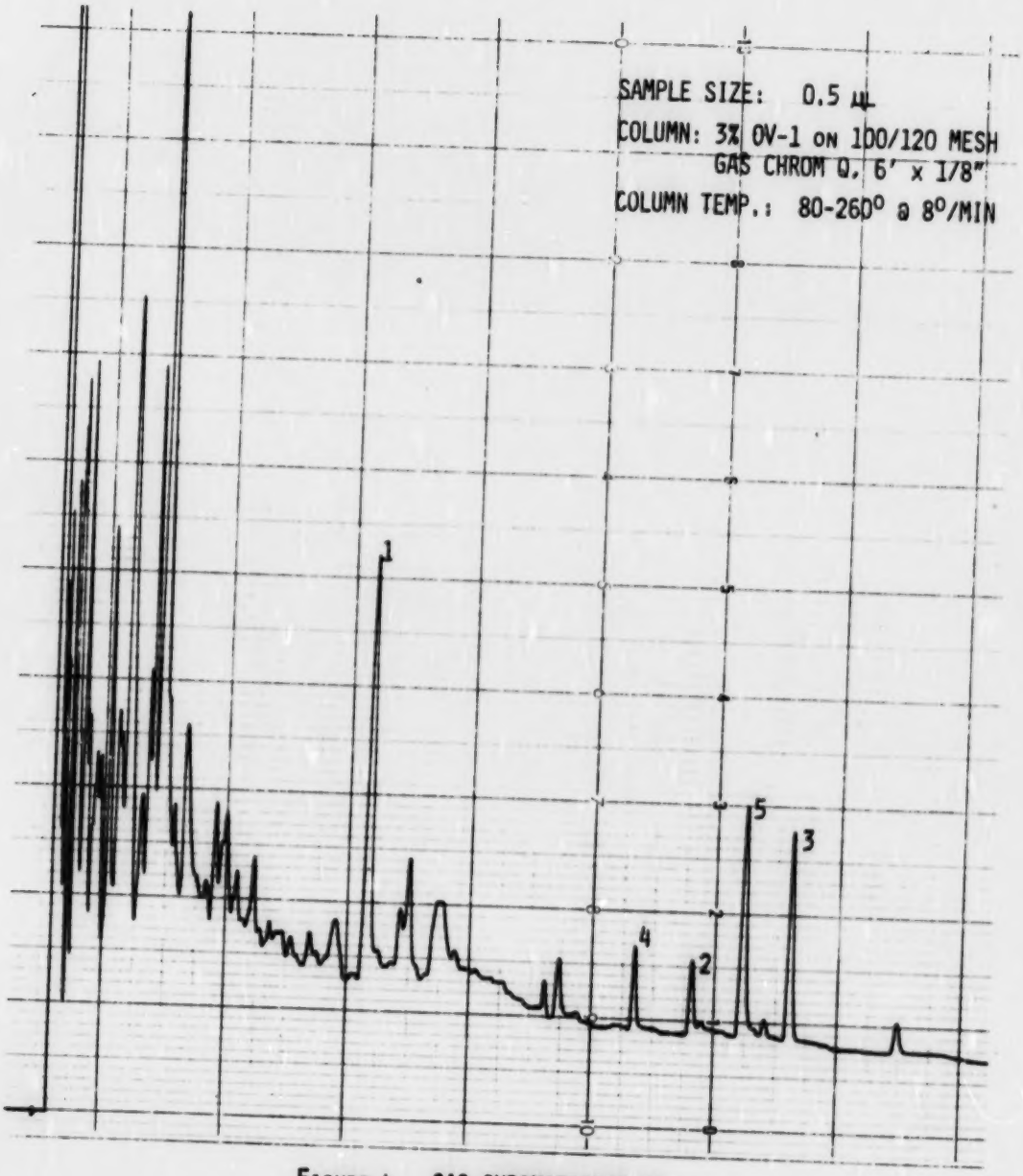

FIGURE 4. GAS CHROMATOGRAM OF CCE311, LANDFILL WELL

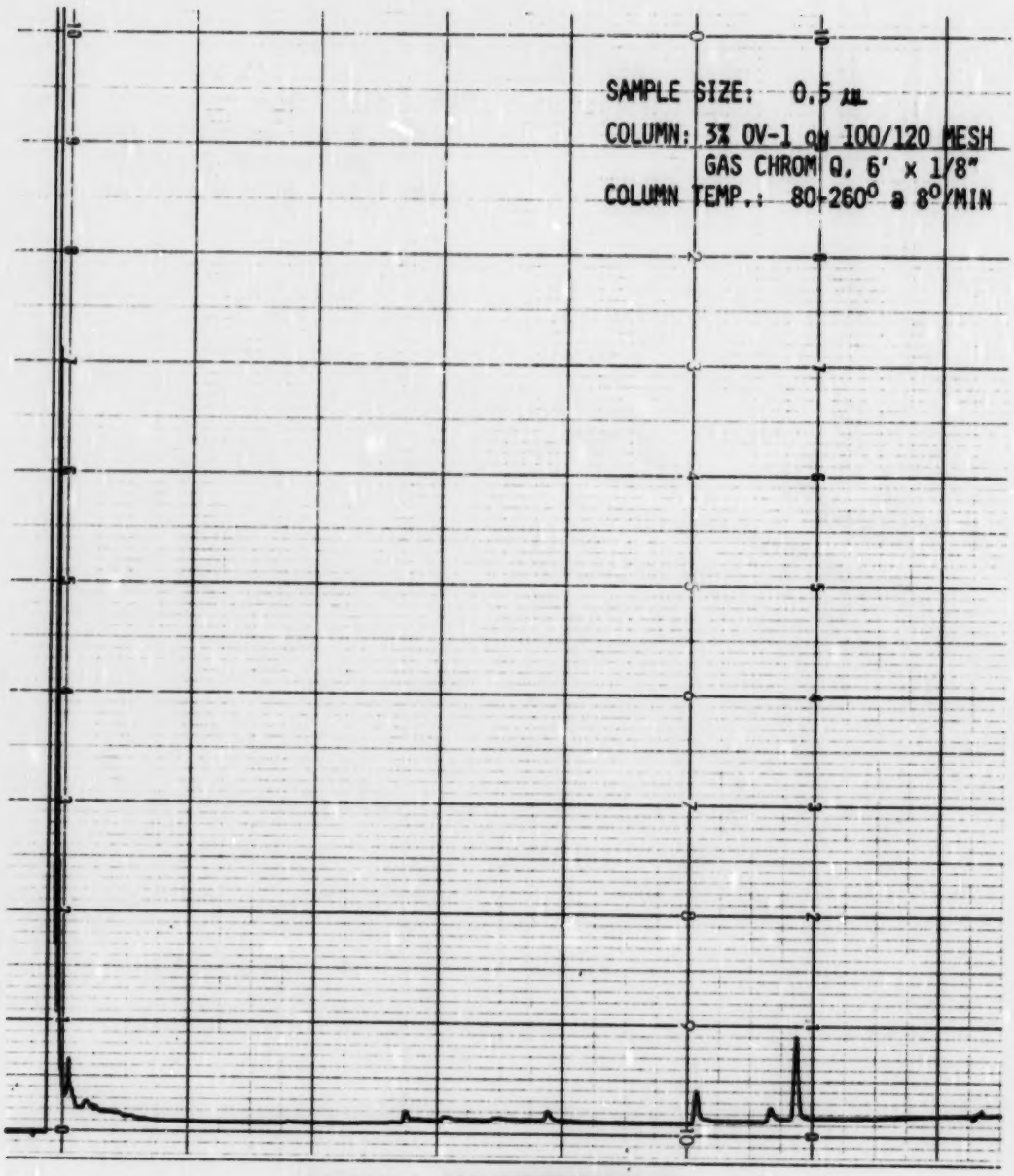

FIGURE 5. GAS CHROMATOGRAM OF CCEC, CONTROL WELL

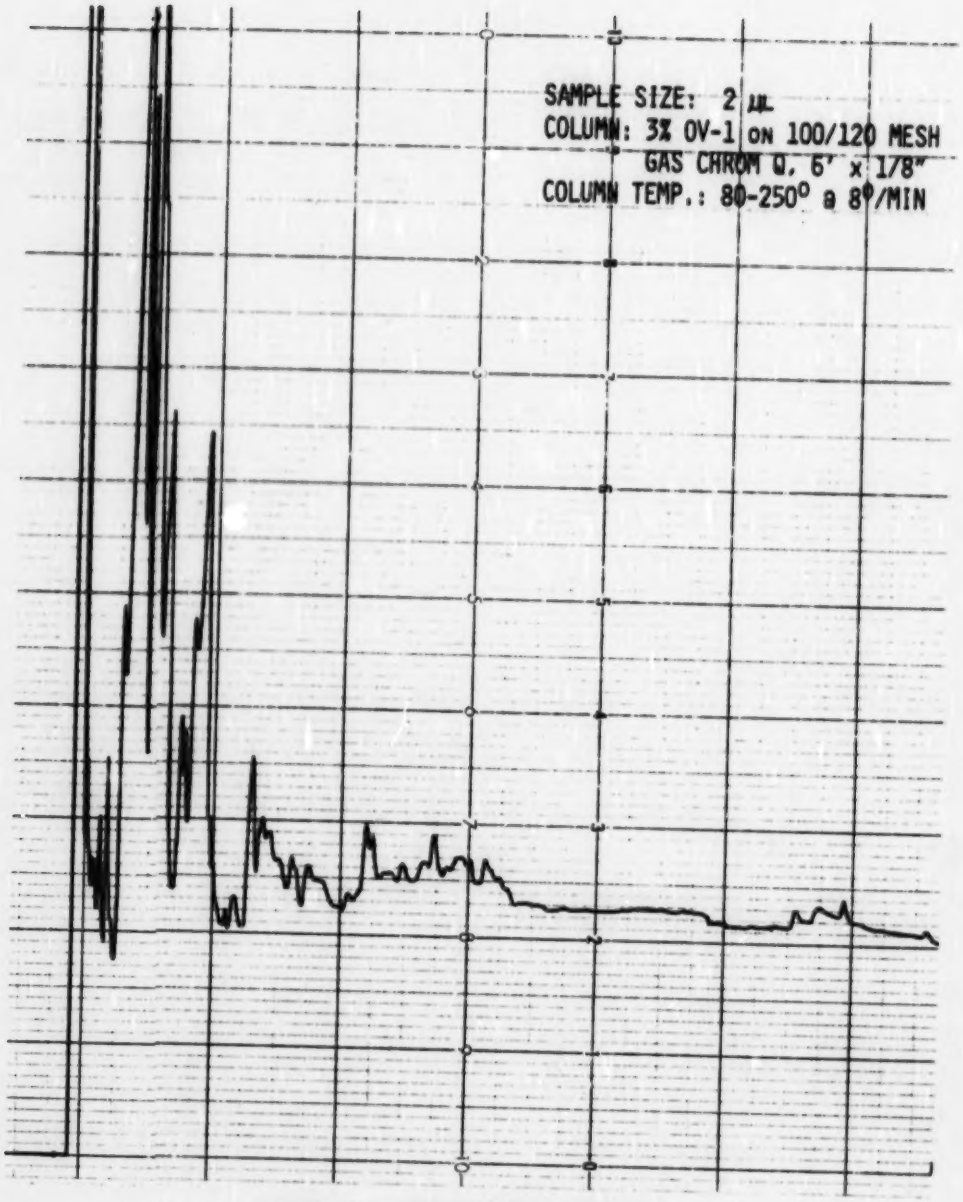

FIGURE 6. GAS CHROMATOGRAM OF CAE3II, LANDFILL WELL

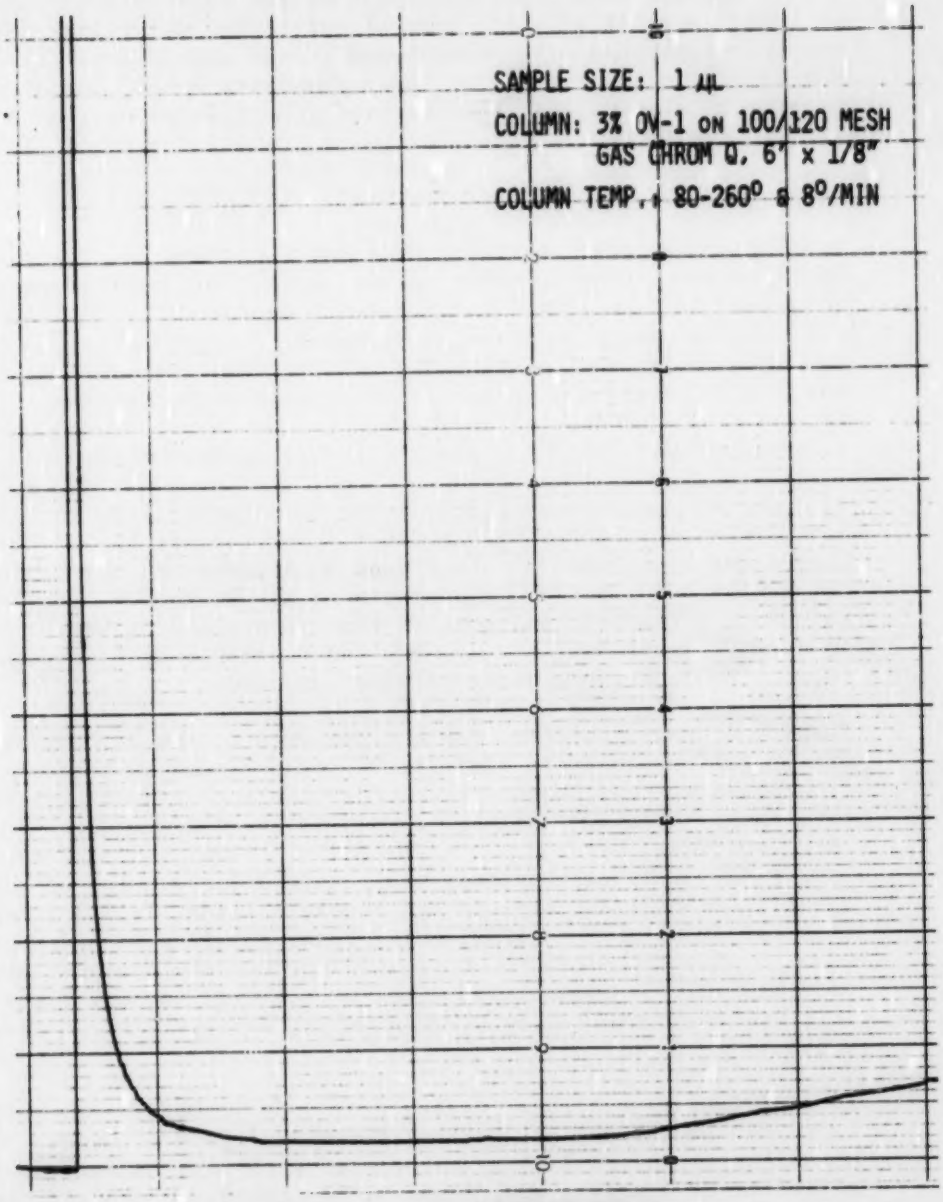

FIGURE 7. GAS CHROMATOGRAM OF CAEC. CONTROL WELL

It was obvious that practically all of the major organic components of CCE3II and CAE3II which were of sufficient volatility for gas chromatography had been contributed to the ground water by the landfill, and identification of any of these compounds would, therefore, be helpful in elucidating the effect of the landfill on ground water.

Identification of Compounds in CCE3II and CAE3II

Table 6 presents a tabulation of those compounds which were identified in the carbon chloroform and carbon alcohol extracts prepared from ground water from well No. 3. The CCE and/or CAE fraction(s) in which the compound was identified, information concerning the method of identification, and additional pertinent data such as industrial uses and toxicity information are presented for each compound. Also, estimates of the quantities present in the sampled water are given for those compounds for which quantitative evaluations were achieved.

The general structures of all of the compounds listed in Table 6 were established beyond reasonable doubt. However, it should be noted that exact positions of substituent attachment and chain branching were not achieved for a few compounds, such as the two C_3 alkylbenzenes in CCE3II-SG7-SG9→11 and some of the C_7, C_8, and C_9 isomeric acids, because of unavailability of required standards or failure of GC columns to separate closely related compounds.

There was strong evidence for the presence in the various fractions of several compounds in addition to those listed in Table 6, but their structures were not considered sufficiently confirmed for inclusion in this Table. These "possible" compounds and the fractions in which they were found were: a C_8 ketone, CCE3II-SG6; a glycol ether, CCE3II-SG7-SG12; triethyleneglycol ether and a diester of adipic acid, CCE3II-SG7-SG13; and benzoic and nonanoic acids, CAE3II Acids. Also, GC examination of the CAE3II Acids fraction after it had reacted with boron trifluoride-methanol gave evidence for the probable presence of relatively low quantities of C_{12}, C_{14}, C_{16}, and C_{18} fatty acids. This was not confirmed by GC-MS studies, however, due to time limitations.

Some of the major higher boiling compounds in CCE3II, as indicated by number on the chromatogram pictured in Figure 4, were: 1, diethyl phthalate (4 µg/1); 2, butylcarbobutoxymethyl phthalate; 3, dioctyl phthalate (2.4 µg/1); and, 4 and 5, the compounds tentatively identified as a triethyleneglycol ether and a diester of adipic acid. Diacetone alcohol (10.9 µg/1), p-cresol (8.6 µg/1), cyclohexanol (1.0 µg/1), camphor (0.9 µg/1), and o- and p-xylene (0.6 and 0.9 µg/1, respectively) were the major lower boiling compounds identified in this CCE, but no attempt has been made to indicate these compounds in Figure 4 because of the complexity of the early portion of the chromatogram.

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code [a]	Remarks
Fenchone	0.2	CCE3II-SG4	SR	Used as a "generally regarded as safe" (GRAS) flavoring;[19] present in paper mill's raw waste.[20]
Camphor	0.9	CCE3II-SG4	SR	Used as a plasticizer for cellulose esters and ethers; moth and mildew preventive; flavoring.[19] Neoplastic effects produced experimentally in rats.[21]
2,6-di-Tertiarybutyl Benzoquinone	-	CCE3II-SG4	CS(0.874)	Hydroquinone precursor is used as an antioxidant; polymerization catalyst.[19]
Diethyl Phthalate	4.1	CCE3II-SG4	SR	Used as a plasticizer; solvent for cellulose acetate; camphor substitute; perfume fixative; wetting agent; insecticides; alcohol denaturant.[19] Bitter taste; moderately toxic when ingested.[21]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code[a]	Remarks
2,6-di-Tertiaryamyl Benzoquinone	-	CCE3II-SG4	CS(0.321)	Hydroquinone precursor is used as an antioxidant; polymerization catalyst.[19]
Diisobutyl Phthalate	0.1	CCE3II-SG4 and CCE3II-SG7-SG4→6	SR	Used as a plasticizer.[19]
Di-n-Butyl Phthalate	-	CCE3II-SG4	SR	Used as a plasticizer; polymerization catalyst; oxidant.[19] Oral toxic dose in man, 140 mg/kg produces central nervous system effects.[21]
Butylcarbobutoxy-methyl Phthalate	-	CCE3II-SG4	SI	Used as a plasticizer.[19]
Butylbenzyl Phthalate	-	CCE3II-SG4	SI	Used as a plasticizer for polyvinyl and cellulose resins.[19]
Dicyclohexyl Phthalate	0.2	CCE3II-SG4	SR	Used as a plasticizer for rubber, polyvinyl chlorides, and other polymers; mildly aromatic odor.[19]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code[a]	Remarks
Dioctyl Phthalate[c]	2.4	CCE3II-SG4	SR	Used as a plasticizer for polyvinyl chlorides and other vinyls. Slight odor.[19]
p-Cresol	14.6	CCE3II-SG5 and CAE3II Acids	SR	Used as an active constituent of creosote.[19]
o-Xylene	0.6	CCE3II-SG7-SG7	SR	Used in manufacture of phthalic anhydride; insecticides; motor fuels; dyes.[19] Moderately toxic.[19]
p-Xylene	0.9	CCE3II-SG7-SG7	SR	Used in synthesis of terephthalic acid for polyester resin synthesis (dacron, mylar, etc); insecticides. Moderately toxic.[19]
Cyclohexanol	1.0	CCE3II-SG7-SG7	SR	Used in making phenolic insecticides; lacquer polishes; plastics; germicides; source of adipic acid for nylon manufacture.[19]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code [a]	Remarks
N-Ethyl-p-Toluenesulfonamide	0.1 [b]	CCE3II-SG7-SG8	SI	Used as a plasticizer. Moderately toxic.[19]
N-Ethyl-o-Toluenesulfonamide	-	CCE3II-SG7-SG8	SI	Used as a plasticizer. Moderately toxic.[19]
C_3 Alkylbenzenes [c] (2 compounds)	-	CCE3II-SG7-SG9→11	SI	C_3 alkylbenzene isomers are found in American petroleum.[22]
Diacetone Alcohol	10.9	CCE3II-SG7-SG9→11	SR	Used as a solvent for cellulose acetate, various oils, resins, dyes, tars, and waxes; also used in hydraulic compression fluids; wood preservatives; and metal cleaning.[19]
Butoxyethanol	-	CCE3II-SG7-SG9→11	SR	Used as a solvent for nitrocellulose resins, sprays, lacquers, and enamels.[19] Oral LD_{50} for rats is 470 mg/kg.[21]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code [a]	Remarks
Ethyl Carbamate	-	CCE3II-SG7-SG9→11	CP	Used as a solvent for various organics; solubilizer and cosolvent for pesticides, fumigants, and cosmetics.[22] Proved experimentally to be carcinogenic.[21]
Tri-n-Butyl Phosphate	1.7	CCE3II-SG7-SG9→11	SR	Used as a plasticizer; antifoam agent; solvent for nitrocellulose, cellulose acetate, heat exchange medium; dielectric.[19] Moderately toxic by ingestion.[19]
p-Toluenesulfonamide	-	CCE3II-SG7-SG12	CP	Used as a plasticizer; fungicide; mildewicide in paints; also resin synthesis. Oral LD_{50} in birds is 75 mg/kg.[22]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code[a]	Remarks
Methyl Pyridine	-	CCE3II-SG7-SG12	CS(0.504)	Comes from dry distillation of coal and bones. Used in insecticide manufacture; dyes; rubber; used as solvent; and in making vinyl pyridine.[19] Moderately toxic, strong unpleasant odor.[19]
N,N-Diethylformamide	-	CCE3II-SG7-SG12	CP	Used in rubber manufacture.[20]
Triethylphosphate	0.3	CCE3II-SG7-SG12	SR	Used as a plasticizer for resins, plastics, gums; pesticide manufacture; catalyst; solvent; lacquer remover.[19] Highly toxic, causes cholinesterase inhibition.[22]
Bis-2-Hydroxypropyl-ether	-	CCE3II-SG7-SG21	CP	A dimerization product of propylene glycol which is used as a non-toxic antifreeze in dairies and breweries; a substitute for ethylene glycol and manufacture of synthetic resins.[22]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code[a]	Remarks
3-Methylcyclopentan-1,2-Diol	-	CCE3II-SG7-SG21	CS(0.755)	
Acetic Acid	-	CAE3II Acids	SR	Used in manufacturing plastics, insecticides, vinyl acetate, and photographic chemicals;oil well acidizing and food additive. Pungent odor.[22]
Isobutyric Acid	48.7	CAE3II Acids	SR	Used in the manufacture of esters for solvents, flavors, and perfumes; disinfection; tanning agent; deliming hides. LD_{50} in rats is 280 mg/kg.[19] Pungent odor like that of butyric acid, but not so unpleasant, mild irritant.[22] Detection of odor in water at 8.1 mg/l and of taste in water at 1.6 mg/l.[23]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water g/l	Fraction	Identification code[a]	Remarks
Butyric Acid	1.5	CAE3II Acids	SR	Used as an emulsifying agent; disinfectant; gasoline sweetener; perfume ester preparation and deliming agent.[19] Neoplastic effects have been produced in rats.[21] Obnoxious odor.
Isovaleric Acid	0.7	CAE3II Acids	SR	Used in flavors, perfumes, and manufacture of sedatives.[22] Occurs in tobacco and several other plants; also, occurs in hop oil. Acid taste, disagreeable rancid-cheese odor. Detection of odor in water at 0.7 mg/l.[23]
Valeric Acid	1.1	CAE3II Acids	SR	Used as an intermediate in perfumery. Unpleasant odor.[22]

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compounds	Estimated concentration in ground water g/l	Fraction	Identification code[a]	Remarks
2-Ethylhexanoic Acid	4.2	CAE3II Acids	SR	This acid is a typical low to medium weight isoacid. Salts used for varnish driers, heat stabilizers for vinyl resins, greases, as thickening agents in certain lacquers and paints, inhibition of sludge, and varnish deposition in mineral oils. Compound itself used as a plasticizer and in alkyd resins.[24]
Isomeric C_6 Acid[c]	17.1[d]	CAE3II Acids	SI	Refer to 2-ethylhexanoic acid above, which has similar characteristics.
Isomeric C_6 Acid[c]	0.2[d]	CAE3II Acids	SI	Refer to 2-ethylhexanoic acid above, which has similar characteristics.
Isomeric C_7 Acid[c]	7.5[e]	CAE3II Acids	SI	Refer to 2-ethylhexanoic acid above, which has similar characteristics.

Table 6: COMPOUNDS IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water µg/l	Fraction	Identification code[a]	Remarks
Isomeric C_8 Acid[c]	-	CAE3II Acids	SI	Refer to 2-ethylhexanoic acid above, which has similar characteristics.
Cyclohexanecarboxylic Acid	2.8	CAE3II Acids	SR	Used in insecticide formulation; as a stabilizer for vulcanized rubber; paints and varnishes; lubricating oils; dry cleaning soaps.[19]
Caprylic Acid	0.6	CAE3II Acids	SR	An intermediate in the manufacture of esters used in perfumery; in manufacture of dyes. Slightly unpleasant rancid taste.[22]
Caproic Acid	1.1	CAE3II Acids	SR	Used in the manufacture of esters for artificial flavors and of hexyl derivatives, especially hexylphenols, hexylresorcinol, etc.[22] Characteristic goat-like odor.[22]

Table 6: COMPOUND IDENTIFIED IN CCE3II AND CAE3II (Continued)

Compound	Estimated concentration in ground water g/l	Fraction	Identification code[a]	Remarks
Heptanoic Acid	1.0	CAE3II Acids	SR	Found in the various fusel oils in appreciable amounts. Has been observed in rancid oils. Disagreeable, rancid odor.[22]

a SR - Comparison with standard (MS and GC).
CP - Good comparison with standard spectrum plotted from NIH library of mass spectra.
CS - Matching with high similarity index from Batelle library of mass spectra.
SI - Interpretation of mass spectrum - consistent with spectra of known similar compounds.

b Determined as N, N-dimethyl-p-toluenesulfonamide.

c General structure confirmed beyond reasonable doubt, but position of substitution or chain branching not determined because necessary standards were unavailable or compounds were not separated by G.C. columns employed.

d Determined as 2-ethylbutyric acid, but probably is not this compound.

e Determined as n-heptanoic acid.

CCE3II, like CCE3 in the initial phase of study, was found to contain elemental sulfur. However, in marked contrast to the rather complex mixture of aliphatic hydrocarbons noted in the hexane fractions obtained by silica gel column chromatography of CCE's 2 and 3 in the initial phase of study, essentially no organic compounds were found in the silica gel hexane fractions from CCE3II, and no evidence for the presence of significant levels of aliphatics was noted in any other fractions prepared from this CCE. This may indicate major differences in the organic components contributed to ground water by the landfill at the different times of sampling for the two phases of study, although other compounds identified in the first phase of study such as the phthalic esters, were essentially the same as those found in the later work. Sampling anomalies resulting from the tendency of the very water-insoluble aliphatic hydrocarbons to agglomerate and separate from water could possibly be involved, but this seems unlikely. The loss of aliphatic hydrocarbons during sample preparation in the second phase of study is virtually precluded as a possibility because of the success achieved during this phase in recovering substances of higher volatility than the aliphatics found in the initial study. The possibility that the aliphatic hydrocarbons found in the initial phase of study were contaminants introduced in obtaining and processing CCE's cannot be completely eliminated. However, the presence of aliphatic hydrocarbons in most landfills would not be unexpected.

The major compounds readily amenable to gas chromatography in CAE3II were relatively low boiling, as shown by the chromatogram in Figure 4. The principal compounds identified in this extract and their estimated concentrations in the sampled ground water were: isobutyric acid (48.7 µg/l); an isomeric C_6 acid (17.1 µg/l); an isomeric C_7 acid (7.5 µg/l); 2-ethylhexanoic acid (4.2 µg/l), and p-cresol (6.0 µg/l).

A few of the compounds identified by this study as pollutants contributed to ground water by the Norman landfill could be leachates of natural products, including foods, or possibly end products of microbial metabolism of organic compounds. For example, the short chain, normal carboxylic acids are found in many foods and plants; acetic and butyric acids are common end products of anaerobic metabolism of carbohydrates; and phenolic substances are ubiquitous phytochemicals. As Table 6 indicates, however, practically all of the identified compounds are employed industrially in the manufacture of a wide array of products for domestic and commercial use which are likely to ultimately find their way to landfills. The phthalic acid esters are a case in point. These compounds are used very extensively as plasticizers for production of polymers employed in such diverse products as food wrap film, garden hose, upholstery, electrical insulation, and clothing. Such products are almost undoubtedly the source of the phthalates contributed to ground water by the Norman landfill. Hence, although the Norman landfill receives hardly any industrial wastes directly, leaching of manufactured products deposited in this landfill

is apparently responsible for introduction of pollutants commonly associated with industrial wastes into ground water underlying and within the landfill.

The compounds identified in this study, while appearing to comprise a major portion of those substances which were readily amenable to gas chromatography in CCE3II and CAE3II, were actually present in ground water from well No. 3 only in very low concentrations. The sum of the concentrations in the ground water of all the compounds obtained from CCE3II and CAE3II was 125 µg/l. Even if the concentrations of those compounds which were identified,but for which no quantitative data were obtained,could be added to this value it would still be relatively low. However, in evaluating the significance of the quantitative data obtained in this work it should be noted that these data must be considered minimum values because of quantitative inadequacies of the carbon adsorption method. These inadequacies result because: activated carbon may fail to quantitatively adsorb dissolved organic compounds from sampled water; complete recovery of adsorbed compounds from the activated carbon may not be accomplished during extraction; and, volatile sample components may be lost during drying of the activated carbon. This is illustrated by comparing the total combined weight of CCE3II and CAE3II, 2.012 mg/l, with the average TOC value for water from well No. 3 of 13.4 mg/l during the period August 1973 to May 1974. Obviously, less than 10 percent of the organic matter present in the sampled ground water was recovered in the CCE and CAE if the organic equivalent of 13.4 mg carbon/l is considered. Much of this loss may reflect the failure of macromolecular material to be adsorbed on the activated carbon column and/or the irreversible adsorption of highly polar compounds on the carbon. A considerable loss of compounds which should have appeared in the CCE and CAE as components amenable to gas chromatography may well be indicated, however, and the actual concentrations in the ground water of the compounds identified in this study may be much higher than indicated.

As previously noted, the low total organic carbon values for ground water in the landfill and the history of the Norman landfill both indicate that initial extensive leaching and subsequent stabilization of refuse in the studied area of the landfill probably had occurred before this investigation was begun. Hence, the compounds identified in this study probably are substances which are leached very slowly from the refuse in the landfill and/or substances which persist for considerable periods of time in the aquifer in the vicinity of the refuse from which they were leached because of sorption on the earth solids comprising the aquifer. This observation implies the potential for long-term insidious pollution of ground water by undesirable organic chemicals from landfills. Slowly decaying domestic and commercial products in landfills would appear likely to serve as reservoirs feeding low levels of industrial organic pollutants into aquifers for many years after the

landfills have been closed and forgotten. Even those substances which are sorbed relatively strongly on aquifer solids could ultimately pose a pollution threat if they were resistant to biochemical and abiotic degradation in the ground water environment. Such compounds could move as zones by slow, "chromatographic" migration to finally reach wells providing water for consumption by humans or domestic animals. Because of the low levels of pollutants likely to be involved, physical properties of the polluted ground water would probably not be altered sufficiently to indicate the presence of the offending compounds. This presence could be a matter of considerable concern, however, since the health effects of chronic ingestion through water of even very low levels of compounds such as those identified in this study are largely unknown. This, coupled with the great difficulty involved in removing pollutants, particularly those which tend to adsorb significantly on aquifer solids, from a polluted aquifer, dictate the need for further investigation of this potential problem. In particular, information concerning the mobility and longevity in the ground water environment of compounds such as those in Table 6 are needed. The observation in the initial phase of study that water in well No. 2, outside the landfill, contained the same phthalic acid esters as water from well No. 3, within the landfill, seems to indicate movement of these substances in the aquifer, particularly since well No. 2 sampled only water in the lower 10 ft of the aquifer. Information of this type is, however, generally very scarce.

Although many of the major organic compounds of CCE3II and CAE3II that were readily amenable to gas chromatography were identified during this study, the major portions of these extracts were not characterized. The weight of CCE3II was 402 µg/1, and that of CAE3II was 1610 µg/1, while the total weights of the compounds identified in these extracts were only 32 µg/1 and 93 µg/1, respectively. Much of the missing material may be accounted for in CCE3II-SG7-SG20↔26 fractions, and in CAE3II-ether insolubles, water solubles, and acids fractions; it was probably composed to a large extent of compounds that were too polar and/or too high in molecular weight to yield readily to gas chromatography. Had time permitted, study of these fractions by preparation of suitable derivatives for analysis by gas chromatography and utilization of liquid chromatography procedures would probably have yielded much additional information concerning the organic pollutants contributed to ground water by the landfill investigated.

SECTION VI

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